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Journal of Inorganic Biochemistry 99 (2005) 1945–1951
Journal of Inorganic Biochemistry
www.elsevier.com/locate/jinorgbio

Investigation on the complex of diperoxovanadate with 2-(2′-pyridyl)-imidazole

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Received 28 February 2005; received in revised form 21 May 2005; accepted 10 June 2005
Available online 25 July 2005

Abstract

A novel diperoxovanadate complex $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-pyridyl})\text{-imidazole}\}]\cdot 4H_2O$ was synthesized in aqueous solution under physiological conditions. The solution structure of the complex was characterized by multinuclear (^1H, ^{13}C, ^{14}N, and ^{51}V) as well as multi-dimensional (DOSY and C-H COSY) NMR techniques in the interaction system of $NH_4VO_3/H_2O_2/2\text{-}(2'\text{-pyridyl})\text{-imidazole}$ at room temperature. The crystal structure of the complex was determined at 173 K by single-crystal X-ray diffraction method. It belongs to the monoclinic space group $P21/c$ with $a = 13.048(4)$, $b = 6.984(2)$, $c = 17.814(5)$ Å, $\beta = 104.695(5)$, $V = 1570.3(8)$ Å^3 and $Z = 4$. The crystal is composed of ammonium ions, {2-(2′-pyridyl)-imidazole}oxodiperoxovanadate(V) ions, and water molecules, which are held together by ionic and hydrogen bond forces. The metal atom in the complex is seven-coordinated with a distorted pentagonal bipyramidal geometry. It is the first mononuclear diperoxovanadate complex with a *N*, *N*′-chelating biheteroaromatic ligand and its ^{51}V chemical shift is at the highest field among the known mononuclear diperoxovanadate(V) complexes.

Keywords: Diperoxovanadate; Crystal structure; 2-(2′-Pyridyl)-imidazole; Interactions; NMR

1. Introduction

Vanadate compounds were reported to be a new kind of powerful insulin mimic and anticancer agents based on their biological response both in vitro and in vivo and may be developed into new oral drugs for diabetes and tumor [1–10]. It is therefore not surprising to see that coordination chemistry and biological mechanism of vanadate compounds have recently encouraged many interests [9–22]. For example, Orvig et al. have synthesized and characterized many vanadium (III,IV,V) complexes and studied their insulinomimetic activities [18–24]. After the pioneer work of Orvig and co-workers, similar work was carried out by Mahroof-Tahir et al. [7,8] using different ligands. Abu-Omar et al. [9,10] have studied the kinetics and mechanisms of ligand substitution reactions of bisperoxovanadium(V) compounds at physiological pH and the relevance to their DNA-cleavage activities. Kiss et al. [11–13] have characterized the vanadium (IV,V) complexes in aqueous solution by several spectroscopies. Pratt et al. [14–16] have investigated the formation and structure of complexes between hydroxamic acids and vanadate at neutral pH and their mechanism of inhibition of the β-lactamase. Among these studies, detailed and thorough spectroscopic investigations on the interaction systems between peroxovanadate complexes and organic ligands have been performed [25–30]. Several diperoxovanadate complexes, such as $M_n[OV(O_2)_2L]\cdot mH_2O$ (where M = NH_4^+, K^+, Na^+; n = 1–3; m = 1–5; L = ligand with C_2

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doi:10.1016/j.jinorgbio.2005.06.007

symmetry, for examples: 2,2′-bipyridine, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline), have been synthesized [37]. It is found that pyridine (abbr. Py) is one kind of important building blocks for peroxovanadate compounds [37] and imidazole (abbr. Imi) has strong coordinative ability [26,28,30,32,35]. Therefore, 2-(2′-pyridyl)-imidazole [abbr. 2-(2′-Py)-Imi], which has both the pyridine and imidazole group, is expected to be a good ligand for formation of peroxovanadate coordination compounds. Based on this consideration, a new peroxovanadate complex $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]\cdot 4H_2O$ was synthesized through the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi in aqueous solution under physiological conditions. Its structure was characterized by solution NMR and single-crystal X-ray diffraction. The structure and spectroscopic properties of the diperoxovanadate species in solution were studied by 2D NMR diffusion ordered spectroscopy (abbr. DOSY) as well as by 1D ^{1}H, ^{13}C, ^{14}N, and ^{51}V NMR. Through the combination use of these methods, a better understanding of the species was achieved. It is the first mononuclear diperoxovanadate complex with a *N*,*N*′-chelating biheteroaromatic ligand and its ^{51}V chemical shift is at highest field among the known mononuclear diperoxovanadate complexes in the literature.

2. Experimental

2.1. Materials and preparation

The compounds NH_4VO_3, H_2O_2, D_2O, NaCl, Py, and Imi were analytic grade reagents. 2-(2′-Py)-Imi shown in Fig. 1 was synthesized according to the literature [38]. To form the ternary system of NH_4VO_3/H_2O_2/L (where L = Py, Imi, and 2-(2′-Py)-Imi), NH_4VO_3 and H_2O_2 were first mixed in D_2O solution to produce the species $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(H_2O)]^-$ (abbr. bpV), then L was added to the solution. The ionic medium was chosen to represent physiological conditions, 0.15 mol/L NaCl D_2O solution at 298 K in all NMR measurements.

The diperoxovanadate complex was prepared by adding 10 mL H_2O_2 (30%, w/v, solution) and 1.16 g NH_4VO_3 (10 mmol) to 50 mL distilled water. After the NH_4VO_3 was dissolved, 1.46 g 2-(2′-Py)-Imi (10 mmol) was added to the mixture. The mixture was stirred in cooled ice water bath at 273 K for 2 h. After that, ethanol was added gradually until a precipitate appeared. The reaction mixture was then filtered and the solution was kept at 283 K for a week to crystallize. The crystals were filtered and washed with 2 mL cold water and 7 mL cold ethanol (three times) and then dried on a filter paper. The isolated yield was 73% based on the vanadate. Anal. Calcd. for $NH_4[OV(O_2)_2(C_8H_7N_3)]\cdot 4H_2O$ ($C_8H_{19}N_4O_9V$): C, 26.24%; H, 5.23%; N, 15.30%. Found: C, 26.11%; H, 5.05%; N, 15.41%. IR (KBr): $v = 3498$ vs (>N–H), 3195 vs, 2916 vs, 2757 vs (H_3N^+–H), 1654 m, 1477 s, 1453 m, 1401 m, 1291 w, 1159 m, 974 m, 940 s (V=O), 923 m, 882 m $(O–O)_{peroxo}$, 863 s $(O–O)_{peroxo}$, 790 m, 750 m, 707 m, 627 m $(V–O_{peroxo})$, 588 s $(V–O_{peroxo})$ cm^{-1}. Raman: $v = 974$ s (V=O), 884 s $(O–O)_{peroxo}$, 632 m $(V–O_{peroxo})$, 588 m $(V–O_{peroxo})$, 494 vs $(V–O_{peroxo})$ cm^{-1}. ^{1}H NMR (D_2O): 7.26 (t, $J = 5.9$ Hz, 1H), 7.47 (s, 1H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.75 (s, 1H), 7.82 (t, $J = 7.7$ Hz, 1H), 8.05 (s, 1H) ppm; ^{13}C NMR (D_2O): 149.0, 147.4, 145.1, 141.1, 132.9, 127.0, 123.9, 121.2 ppm.

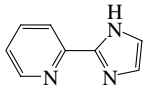


Fig. 1. Structure of 2-(2′-pyridyl)-imidazole.

2.2. Spectroscopy

All NMR spectra were recorded on Varian Unity plus 500 spectrometer operating at 500.4 MHz for ^{1}H, 125.7 MHz for ^{13}C, 36.12 MHz for ^{14}N, and 131.4 MHz for ^{51}V NMR. The solvent for ^{1}H, ^{13}C, ^{14}N, and ^{51}V spectra was D_2O. DSS [3-(trimethylsilyl)-propanesulfonic acid sodium salt] was used as an internal reference for ^{1}H and ^{13}C chemical shifts. ^{14}N and ^{51}V chemical shifts were measured relatively to the external standard $MeNO_2$ and $VOCl_3$, respectively, with upfield shifts considered negative. Signal-to-noise ratios were improved by a line-broadening factor of 2, 50, or 10 Hz in the Fourier transformation of all ^{13}C, ^{14}N, or ^{51}V spectra, respectively. DOSY was recorded using a *z*-gradient probe, which delivered a maximum gradient strength of 30 G/cm. The DOSY gradient compensated stimulated echo spin lock (DGCSTESL) sequence [39] was used for acquiring DOSY spectra. The typical experimental parameters for a DOSY spectrum were as follows: gradient duration $\delta = 3$ ms, gradient strength $G = 3$ G/cm, spin lock time $\tau_{SL} = 1.5$ ms, and time interval $\tau = 3.3$ ms. Diffusion coefficient in NMR was generally achieved by stepwise ramping up of the amplitudes of pulsed field gradients (PFGs), and the diffusion times were optimized for every experiment. The typical time required for a DOSY spectrum was approximately 0.8 h (16 scans, relaxation delay 4 s). Reference deconvolution and baseline correction were used to compensate experimental imperfections for all DOSY spectra.

Raman spectrum of the title complex in aqueous solution was recorded on Labram I confocal microprobe Raman system (Dilor, France). The excitation line is 632.8 nm from a He–Ne laser.

Table 1
Crystal data and structure refinement for $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]\cdot 4H_2O$

Empirical formula	$C_8H_{19}N_4O_9V$
Formula weight	366.21
Temperature (K)	173
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P21/c$
Unit cell dimensions	
a (Å)	13.048(4)
b (Å)	6.984(2)
c (Å)	17.814(5)
β (°)	104.695(5)
Cell volume (Å^3)	1570.3(8)
Z	4
Calculated density (g cm^{-3})	1.549
Absorption coefficient (mm^{-1})	0.681
$F(000)$	760
Crystal size (mm)	$0.19\times0.10\times0.50$
θ Range for data collection (°)	2.36–25.00
Limiting indices	$-12\leqslant h\leqslant 15, -8\leqslant k\leqslant 8, -20\leqslant l\leqslant 21$
Reflections collected/unique [R_{int}]	6914/2608 [0.0399]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2608/13/213
Goodness-of-fit on F^2	1.135
Final R indices [$I>2\sigma$ (I_0)]	$R_1=0.0532$, $wR_2=0.1201$
R indices (all data)	$R_1=0.0632$, $wR_2=0.1242$
Largest diff. peak and hole (e Å^{-3})	0.596 and −0.421

2.3. Crystal structure determination

Determination of the unit cell and data collection for diperoxovanadate compound was performed on a Bruker SMART CCD diffractometer at 173 K. Crystal data and details of the data collection and refinement are collected in Table 1. The structure was solved using direct method implemented in the program SHELXS97. All non-hydrogen atoms were refined using full-matrix least-square procedure on F^2. Anisotropic displacement parameters were assigned to non-hydrogen atoms.

3. Results and discussion

3.1. ^{51}V and ^{14}N NMR studies

In the mixture of NH_4VO_3 and $H_2O_2$with 1:5 molar ratio (0.2 mol/L vanadate concentration), the ^{51}V NMR spectrum had a strong peak locating at −692 ppm, which was assigned to $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(H_2O)]^-$ according to the previous reports [30–36,40–42]. When 0.25, 0.5, 0.75, 1.0, or 2.0 equivalent of 2-(2′-Py)-Imi was added to the solution, respectively, a new single peak appeared at about −784 ppm, which was assigned to a new species $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$. To the best of our knowledge, its chemical shift is at the highest field among the known mononuclear diperoxovanadate(V) compounds. The intensity of the new peak increased with the increasing of the quantity of ligand added before reaching a maximum, as shown in Fig. 2. When the equivalent of 2-(2′-Py)-Imi reached 1.0, almost all $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(H_2O)]^-$ converted into the new species. In the meantime, a tiny peak at −732 ppm was found which was assigned to $V(O_2)_3^-$ [43] (see Fig. 2(e)). Generally, the chemical shift of the species $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(H_2O)]^-$ will change a little bit when the solution pH value changes [31,32]. However, Fig. 2 shows that the chemical shift of $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(H_2O)]^-$ hardly changed in this study.

As N atoms are involved in the reaction, $^{14}N/^{15}N$ NMR spectrum may provide some useful information on the interaction system. Since ^{15}N has very low natural abundance (~0.37%) and the residual paramagnetism of vanadium broadens the ^{15}N peaks, the signal-to-noise ratio of ^{15}N spectra is too low to give useful information for the interaction system. Therefore, only ^{14}N NMR shown in Fig. 3 was measured in this work. For the pure 2-(2′-Py)-Imi solution, two ^{14}N peaks appeared at about 295 and 195 ppm, respectively. For the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with 1:5:1 molar ratio (0.2 mol/L vanadate concentration), two ^{14}N peaks of the coordinated 2-(2′-Py)-Imi appeared at about 219 and 157 ppm, which were much more shielded than the free ligand.

To test the stability of the newly-formed species $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$, the ^{51}V NMR spectra of the interaction system were recorded every 24 h at 298 K. During the experimental period (7 days), the ^{51}V peak was unchanged. It means that the new species is rather stable and the spectra obtained from long time

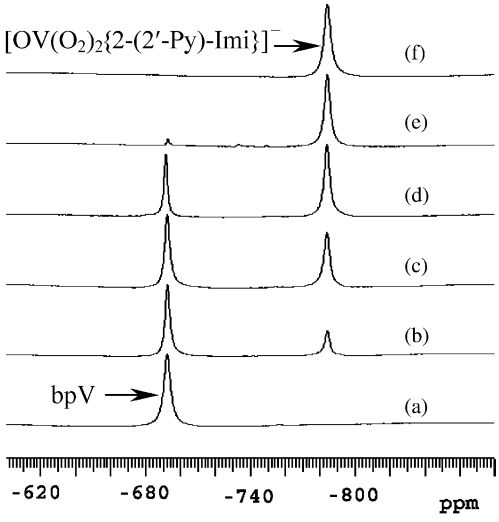


Fig. 2. ^{51}V spectra of the interaction system of NH_4VO_3/H_2O_2/2-(2−-Py)-Imi in aqueous solution with 0.2 mol/L the total concentration of vanadate species. From (a) to (f), the molar ratios of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi are 1:5:0, 1:5:0.25, 1:5:0.5, 1:5:0.75, 1:5:1, and 1:5:2 with pH values 3.5, 4.2, 4.5, 5.0, 6.7, and 7.6, respectively. The bpV refers to the species $[OV(O_2)_2(H_2O)]^-$/$[OV(O_2)_2(D_2O)]^-$.

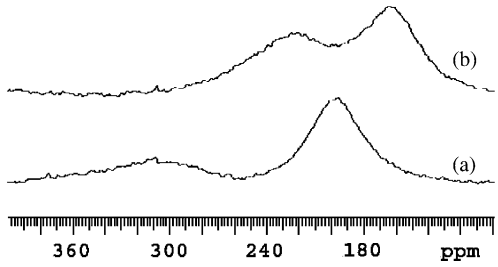


Fig. 3. ^{14}N spectra of the aqueous solution of (a) 2-(2′-Py)-Imi and (b) the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with a molar ratio of 1:5:1 with pH 6.7 and total concentration of vanadate species 0.2 mol/L.

measurements such as ^{13}C–^{1}H COSY and ^{13}C NMR spectra are creditable.

3.2. ^{1}H and ^{13}C NMR spectra

The spectral data are listed in Table 2.

For the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with 1:5:1 molar ratio (0.2 mol/L vanadate concentration), both ^{1}H and ^{13}C NMR spectra had only one group of peaks (see Fig. 4(a) for ^{13}C spectrum), implying that 2-(2′-Py)-Imi was almost coordinated to the central vanadium atom and only one coordination way is present. Increasing the molar ratio of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi to 1:5:2, another group of ^{1}H and ^{13}C peaks appeared (see Fig. 4(b)), which was assigned to the free ligand. Based on ^{14}N NMR spectra shown in Fig. 3, it can be concluded that at least one V–N bond was formed in the interaction system. This nitrogen atom should be in the imidazole ring since it is much easier to form V–N bond than pyridine (see discussion in Section 3.5). When imiazole ligand coordinates to diperoxovanadate forming a six-coordinated complex, the ^{51}V chemical shift of vanadate is about −749 ppm, as reported by Pettersson and Crans [17,26,28,32]. However, the ^{51}V chemical shift of the title complex locates at −784 ppm, which moves to upfield 35 ppm compared with the six-coordinated complex $[OV(O_2)_2(Imi)]^-$. A similar situation can be found in a seven-coordinated complex $[OV(O_2)_2$-(bipy)]$^-$ (^{51}V NMR −746 ppm [26]). Compared with the six-coordinated complex $[OV(O_2)_2(Py)]^-$ (^{51}V NMR −711 ppm [25]), the ^{51}V chemical shift of $[OV(O_2)_2$-(bipy)]$^-$ moves to upfield 35 ppm since there are two pyridine groups coordinating to metal center. Therefore, according to the chemical shifts and the relative areas of the ^{1}H and ^{51}V peaks, we deduced that the two N atoms in the ligand were chelating to the central vanadium atom. Since 2-(2′-Py)-Imi is a *N*,*N*′-chelating biheteroaromatic ligand, theoretically there are two possible ways for it to coordinate to the vanadium atom (isomers **A** and **B** as shown in Fig. 5) [44]. Why only one isomer was observed in our experiments? Which isomer is it? We will come to it in Section 3.5.

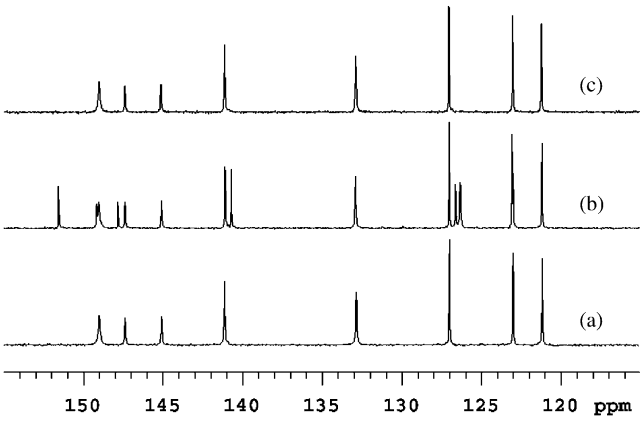


Fig. 4. ^{13}C spectra of the aqueous solution of (a) NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with a molar ratio of 1:5:1 with pH 6.7, (b) NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with a molar ratio of 1:5:2 with pH 7.6, and (c) $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]\cdot 4H_2O$ with pH 6.9. The total concentration of vanadate species is 0.2 mol/L.

3.3. DOSY spectra

The DOSY spectrum of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi (1:5:2, 0.2 mol/L vanadate concentration) in solution is shown in Fig. 6. Except for the solvent, there were two components producing ^{1}H peaks. The component with slower diffusion rate marked by broken line was as-

Table 2
^{1}H and ^{13}C NMR spectral data of the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi in aqueous solution[a]

Species	Chemical shifts (ppm)	
	^{1}H	^{13}C
$[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$[b]	7.24 (t, $J = 5.9$ Hz, 1H), 7.41 (s, 1H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.73 (s, 1H), 7.77 (t, $J = 7.7$ Hz, 1H), 8.05 (s, 1H)	149.0, 147.4, 145.1, 141.1, 132.9, 127.0, 123.0, 121.2
$[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$[c]	7.24 (t, $J = 5.9$ Hz, 1H), 7.41 (s, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.76 (complex, 2H), 8.08 (s, 1H)	149.0, 147.4, 145.1, 141.1, 132.9, 126.9 123.0, 121.1
2-(2′-Py)-Imi[c]	7.22 (s, 2H), 7.35 (t, $J = 5.5$ Hz, 1H), 7.81 (complex, 1H), 7.85 (complex, 1H), 8.47 (d, $J = 3.3$ Hz, 1H)	156.6, 149.2, 147.8, 140.7, 126.6, 126.3, 122.9

[a] The ionic medium is 0.15 mol/L NaCl in D_2O solution at 298 K. The total concentration of vanadate species is 0.2 mol/L.
[b] The molar ratio of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi is 1:5:1 with pH 6.7.
[c] The molar ratio of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi is 1:5:2 with pH 7.6.

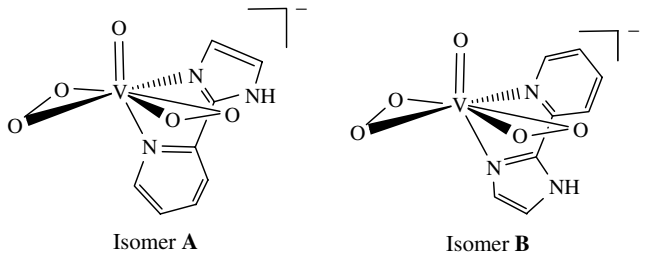


Fig. 5. The possible isomers of $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$.

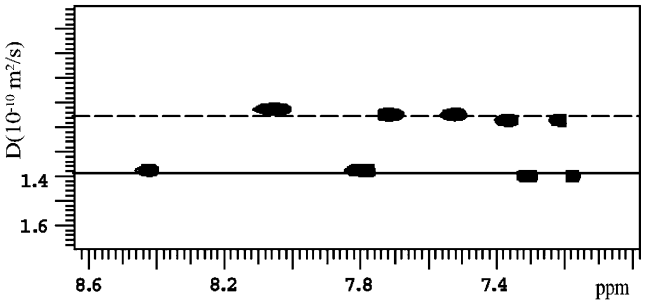


Fig. 6. 2D ^{1}H DOSY spectrum of the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi with a molar ratio of 1:5:2 with pH 7.6 in aqueous solution. The total concentration of vanadate species is 0.2 mol/L. The peaks from free ligand are marked by solid line and the peaks from the newly-formed species $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$ are marked by broken line.

signed to the newly-formed species, $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$. Another component marked by solid lines was assigned to the free ligand. The result of DOSY experiments supports the spectroscopic assignments mentioned above.

3.4. Crystal structure

The crystal of $NH_4[OV(O_2)_2(C_8H_7N_3)]\cdot 4H_2O$ consists of ammonium ions, {2-(2′-pyridyl)-imidazole}oxodiperoxovanadate(V) ions and water molecules. They are held together by ionic and hydrogen bond forces. The content of structure unit is shown in Fig. 7. Bond distances and angles are given in Table 3. The species, $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$, has a distorted pentagonal bipyramidal geometry, which is often observed in transition metal peroxo complexes [1,45,46]. The vanadium atom displaces 0.341 Å from the equatorial plane (defined by O1, O2, O3, O4, and N1 within the limits of experimental error) towards the vanadyl oxygen atom, comparable to approximately 0.3 Å in seven-coordinated diperoxovanadate complexes [47]. The $V\text{–}O_{peroxo}$ bond lengths (1.881–1.918 Å) lie in the range of the normal $V\text{–}O_{peroxo}$ bond distances reported previously [1,45–49]. The lengths of the $(O\text{–}O)_{peroxo}$ (1.449 and 1.462 Å), V=O (1.616 Å), $V\text{–}N_{equatorial}$ (2.103 Å), and $V\text{–}N_{apical}$ (2.360 Å) bonds are in good agreement with the corresponding values reported for other peroxovanadate complexes [1,45–49]. The seven-coordi-

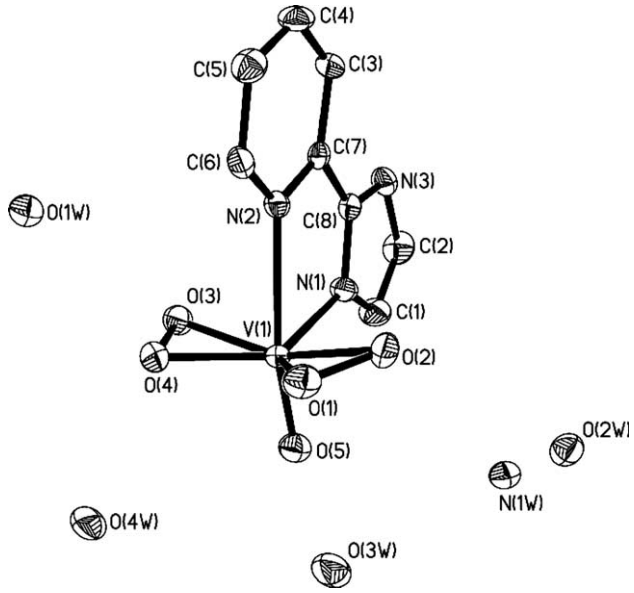


Fig. 7. Structure and numbering scheme of $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]\cdot 4H_2O$.

Table 3
Bond lengths (Å) and angles (°) around the vanadium center in $NH_4[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]\cdot 4H_2O$

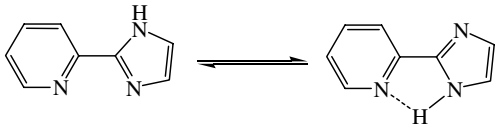
Distance		Angle	
V(1)–O(5)	1.614(2)	O(1)–V(1)–O(2)	45.28(11)
V(1)–O(1)	1.879(2)	O(1)–V(1)–O(3)	132.04(11)
V(1)–O(4)	1.891(2)	O(1)–V(1)–O(4)	88.81(11)
V(1)–O(3)	1.899(2)	O(1)–V(1)–O(5)	103.02(12)
V(1)–O(2)	1.918(2)	O(1)–V(1)–N(1)	132.58(11)
V(1)–N(1)	2.102(3)	O(1)–V(1)–N(2)	85.63(10)
V(1)–N(2)	2.356(3)	O(2)–V(1)–O(3)	159.24(11)
O(1)–O(2)	1.462(3)	O(2)–V(1)–N(1)	88.60(11)
O(3)–O(4)	1.449(3)	O(2)–V(1)–N(2)	78.59(10)
		O(3)–V(1)–O(4)	44.94(10)
		O(4)–V(1)–O(5)	104.46(11)
		O(5)–V(1)–N(1)	93.49(11)
		N(1)–V(1)–N(2)	72.47(10)

nated manner of the vanadium atom verifies our deduction based on NMR study. The chemical shifts of the ^{1}H and ^{13}C NMR spectra of $NH_4[OV(O_2)_2(C_8H_7N_3)]\cdot 4H_2O$ in aqueous solution are the same as those measured from the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi within the limits of experimental error (see Fig. 4 for ^{13}C spectra. The very slight difference of chemical shifts is due to the difference of pH value.), implying that both the $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$ from the interaction system and the dissolved crystal has the same structure.

3.5. Interaction modes

As we have mentioned above, the coordination of 2-(2′-Py)-Imi to $[VO(O_2)_2(H_2O)]^-$ may result in isomers **A**

and **B** (Fig. 5). However, only one isomer was observed in our experiments both in the solution and in crystal state. The determination of crystal structure revealed that the product was isomer **A**. Since the crystal was crystallized from the solution, it is quite possible that the complex has the same coordination manner in solution and in solid state, as reported in Raman study of $K_2[VO(O_2)_2(C_2O_4)]\cdot H_2O$ and $NH_4[VO(O_2)_2NH_3]$ [50,51]. Combined with the conclusion from the ^1H and ^{13}C NMR spectra of $NH_4[OV(O_2)_2(C_8H_7N_3)]\cdot 4H_2O$ in aqueous solution and the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi, we conclude that the structure of $[OV(O_2)_2\{2\text{-}(2'\text{-Py})\text{-Imi}\}]^-$ formed in the interaction system is the same as its crystal structure, which is isomer **A**. In order to explain why only isomer **A** was observed, another two interaction systems, NH_4VO_3/H_2O_2/Imi and NH_4VO_3/H_2O_2/Py, which have been studied systematically [25–28,30,32,35], were used as references. The ^{51}V chemical shifts of $[OV(O_2)_2(Imi)]^-$ and $[OV(O_2)_2(Py)]^-$ are −749 and −711, respectively. Fig. 8 shows the most possible reaction modes of the interaction systems of NH_4VO_3/H_2O_2/Imi and NH_4VO_3/H_2O_2/Py. For NH_4VO_3/H_2O_2/Imi system, imidazole attacks the vanadium atom of $[OV(O_2)_2(H_2O)]^-$ and forms **TS1**. Accompanied by the leaving of water, $[OV(O_2)_2(Imi)]^-$ forms. When the ligand is replaced by pyridine, it undergoes a similar process and forms species $[OV(O_2)_2(Py)]^-$. In the interaction system of NH_4VO_3/H_2O_2/Imi/Py (1:5:1:1 molar ratio, 0.1 mol/L vanadate concentration), the molar ratio between species $[OV(O_2)_2(Imi)]^-$ and $[OV(O_2)_2(Py)]^-$ was determined to be 10:1 from the area ratio of their ^{51}V peaks, implying the much stronger reactivity of imidazole than pyridine. Therefore, for the bidentate ligand 2-(2′-Py)-Imi, it would be much more possible that the nitrogen atom in imidazole ring coordinates to vanadium first and forms **TS1.** Accompanied by the leaving of water, the nitrogen atom in pyridine turns to apical position and forms the second V–N bond. This results in isomer **A**. In addition, an equilibrium exists in 2-(2′-Py)-Imi solution, shown in Fig. 9. Since 2-(2′-Py)-Imi-B has a hydrogen bond and is favorable in energy, it is the dominant species. The domination of 2-(2′-Py)-Imi-B further increases the chance of coordination of imidazole ring due to the existence of hydrogen bond which blocks the coordination of pyridine ring. These may be the reasons that only isomer **A** has been observed.



2-(2'-Py)-Imi-A 2-(2'-Py)-Imi-B

Fig. 9. The equilibrium exists for 2-(2′-Py)-Imi.

4. Conclusions

In this paper, the interaction system of NH_4VO_3/H_2O_2/2-(2′-Py)-Imi under physiological conditions was studied by several NMR techniques. Strong interactions between vanadium atom and 2-(2′-Py)-Imi were observed, indicating the effectiveness of ligands with aromatic nitrogen in the formation of diperoxovanadate complexes. A new diperoxovanadate crystal was obtained. The crystal structure was characterized by single-crystal X-ray diffractometry. This is the first mononuclear diperoxovanadate complex with a *N*,*N*′-chelating biheteroaromatic ligand and its ^{51}V chemical shift is at the highest field among the known mononu-

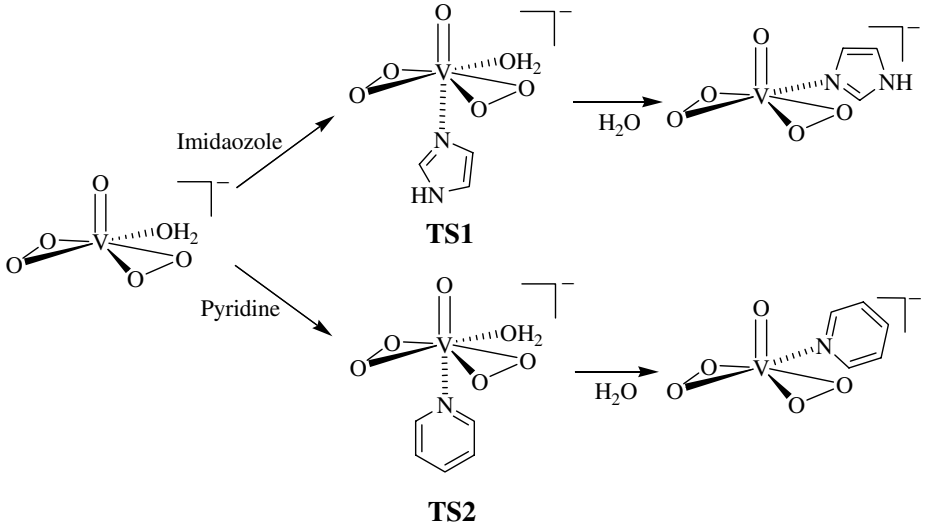


Fig. 8. The possible reaction modes of the two interaction systems, NH_4VO_3/H_2O_2/Imi and NH_4VO_3/H_2O_2/Py.

clear diperoxovanadate complexes reported in literature. Further studies on its insulin-like activity are being carried out.

Obviously, NMR experimental techniques provide a powerful tool to explore the coordinative ways and solution structures of the interaction systems as well as to monitor the formation of new complexes. These methods are being used for further study of the interaction mechanisms between vanadium compounds and organic ligands.

Acknowledgments

This work was supported by Key Project of Health and Science and Technology of Xiamen, United Project of Health and Education of Fujian, NCET and EYTP of Ministry of Education of China, and Returned Oversea Scholar Foundation of Ministry of Education of China.

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